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The location of atoms in Re- and V-containing multicomponent nickel-base single-crystal superalloys

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Abstract

The atomic structure of some Ni-base single-crystal superalloys has been investigated using atom-probe field ion microscopy (APFIM) and the results compared with numerical estimations obtained from the alloy design program (ADP) and the cluster variation method (CVM). Re-containing CMSX4 and V-containing RR2000 alloys, together with TMS63 are the subjects of this study. It is found that Ti, Ta and Hf have a strong preference for the γ' phase, whereas Cr, Co, W, Re and Mo tend to dissolve in the γ phase. V has a very weak preference for the γ phase. The results agree very well with both ADP and CVM. The APFIM analyses have also revealed that Re atoms in CMSX4 tend to preferentially occupy the sites normally designated for Al atoms in the γ' phase. It is demonstrated that the site occupancy of other alloying elements such as Ta, W, Mo and Co can be estimated accurately using CVM, although there are some discrepancies for the distributions of Cr, Ti and Ni. The effect of solute atom distribution on creep properties is discussed briefly.

1. Introduction

Ni-base single-crystal superalloys, which have remarkable properties at elevated temperatures, have been designed for use as turbine blades in aeroengines. In order to develop higher efficiency engines, there are still considerable efforts being devoted to enhance the temperature capabilities of superalloys. Common superalloys consist of γ and γ' phases, which have the face-centred cubic and $L1_2$ structures, respectively. Since the nature and interactions between these two phases to a large extent affect the properties of Ni-base sin-

gle-crystal superalloys, understanding the atomic structure of the γ and γ' phases is of the utmost importance in the development of novel alloys with superior mechanical properties. Atom-probe field ion microscopy (APFIM), which has spatial and chemical resolution at an atomic level, is an appropriate method for investigating the atomic structure of the two phases. Numerical methods have been proposed to predict the atomic structure and mechanical properties of Ni-base superalloys. Harada et al. [1–5] have established an alloy design program (ADP) based on a semiempirical rationalization of available data. It has a demonstrated ability to predict the compositions of the γ and γ' phases, γ/γ' lattice misfits, creep rupture life, etc. As a more fundamental

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approach, Enomoto et al. [6,7] have applied the cluster variation method (CVM) to Ni-base superalloys. This method employs Leonard-Jones pair potentials, and allows the equilibrium phase chemistries, volume fractions and lattice parameters to be estimated as a function of alloy composition, temperature and pressure. Some important factors affecting the mechanical properties of nickel-base superalloys can be estimated with the two methods described above. The present work is an experimental and theoretical investigation of γ and γ' structures in some multicomponent nickel-base single-crystal superalloys containing Al, Ti, V, Cr, Co, Mo, Ta, W, Re, etc. The alloys studied experimentally are Re-containing CMSX4 [8], V-containing RR2000 [9] and TMS-63 [3,5].

2. Experimental procedure

The compositions of the three single-crystal superalloys are shown in Table 1. Among these alloys, CMSX4 and RR2000 are already in commercial use. They were provided by Rolls Royce plc. as 20 mm diameter bars which had been solution heat-treated, followed by a two-step ageing treatment of several hours at about 1400 K and air-cooled, and then 16 h at 1140 K and air-cooled. These samples were cut into $30 \times 15 \times 3$ mm plates, reheated to 1310 K for 185 h in air and then water-quenched. Samples for field ion microscopy were prepared from these plates, their long axes parallel to $\langle 100 \rangle$. They were then electropolished using a standard two-stage process. The first stage utilized a solution of 5% perchloric acid and 25% glycerol in ethanol. The electrolyte for the second stage was 3% perchloric acid in butoxyethanol; the solution was also used during the backpolishing of samples. The

detailed information of the similar heat treatment and sample preparation of TMS63 is described elsewhere [10].

The experiments were performed using the VSW APFIM 200 atom-probe field ion microscope which is equipped with a reflectron-type time-of-flight mass spectrometer with computer control and data acquisition [11]. The sample temperature was maintained at 40 K using a closed-cycle helium refrigerator. To minimize preferential evaporation phenomena, the pulse height fraction and pulse rate were maintained at 20% and 200 Hz, respectively. Detailed description of the layer-by-layer analysis, which allows the determination of the atomic configurations in the γ' phase, is explained later in this paper.

The numerical calculation assumed a material temperature of 1310 K, that is the final heat treatment temperature. Lennard-Jones potential parameters used in the CVM calculations are as in Refs. [6,7], except those for Re and V which were newly evaluated in the same manner as described by Enomoto et al. [6,7].

3. Results and discussions

3.1. Chemical analysis

Fig. 1 shows typical mass spectra of (a) γ and (b) γ' phases in CMSX4. The element peaks are clearly resolved. It should be noted that the average mass resolution, $m/\Delta m$, of Ta^{3+} , W^{3+} and Re^{3+} is maintained at about 1000, even though automatic voltage-controlled analyses were performed in the range 14 to 19 kV, allowing quantitative determination of the compositions with respect to these refractory elements. The two mass spectra related to the γ and γ' phases have distinctive features. Al, Ti, Ta and Hf strongly

Table 1
Chemical composition of superalloys (in at%)

	Ni	Al	Ti	V	Cr	Co	Mo	Hf	Ta	W	Re	C
CMSX4	63.02	12.62	1.27		7.60	9.80	0.38	0.03	2.18	2.12	0.98	0.011
RR2000	57.32	11.01	4.60	1.05	10.56	13.77	1.70					0.09
TMS63	72.0	12.8			7.8		4.6		2.8			

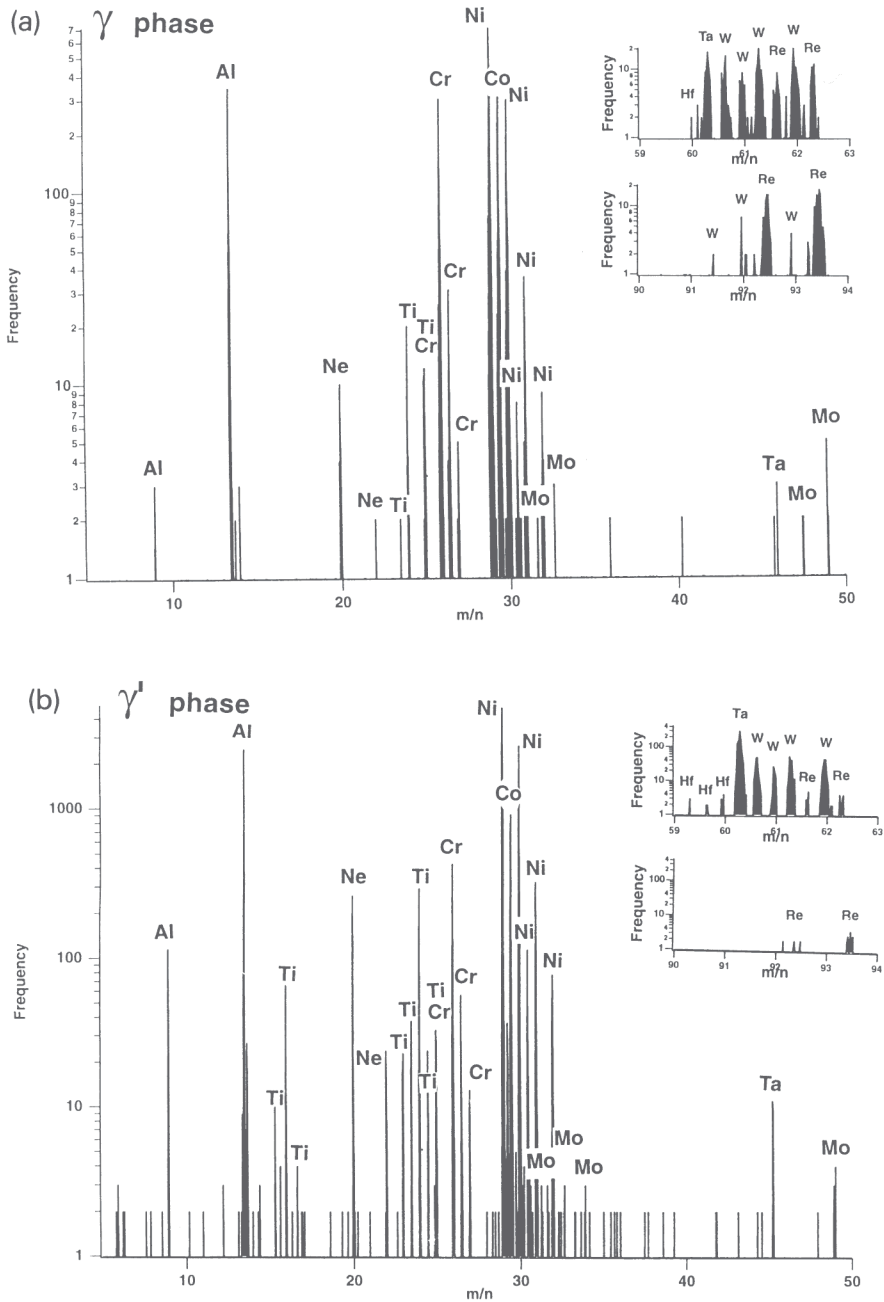


Fig. 1. Typical mass spectra in (a) the γ phase and (b) the γ' phase of CMSX4.

prefer the γ' phase, whereas Co, Cr, Mo, W and Re tend to partition into the γ phase. This is in excellent agreement with published data [12-15]. For RR2000, some carbon ions were detected,

because it contains an exceptionally high carbon concentration. From the limited data, it appears that the carbon atoms have a slight preference for the γ phase. The partitioning tendencies of

other alloying elements in RR2000 are similar to those of CMSX4 and TMS63, except for V which very slightly prefers to partition to the γ phase.

The composition data obtained from CVM and ADP calculations are summarized and compared against experiments in Figs. 2-4. An approximation used for RR2000 is that Co has been treated like Ni in the CVM calculation, due to a lack of appropriate data. This is probably justified since Ni and Co behave similarly in terms of γ/γ' partitioning and site occupation in the γ' phase [6,7]. In spite of the approximation, good agreement is found for the other species in RR2000. It is evident that experiment and theory compare well for CMSX4 and TMS63, as shown in Figs. 2-4.

PHASE COMPOSITION OF RR2000

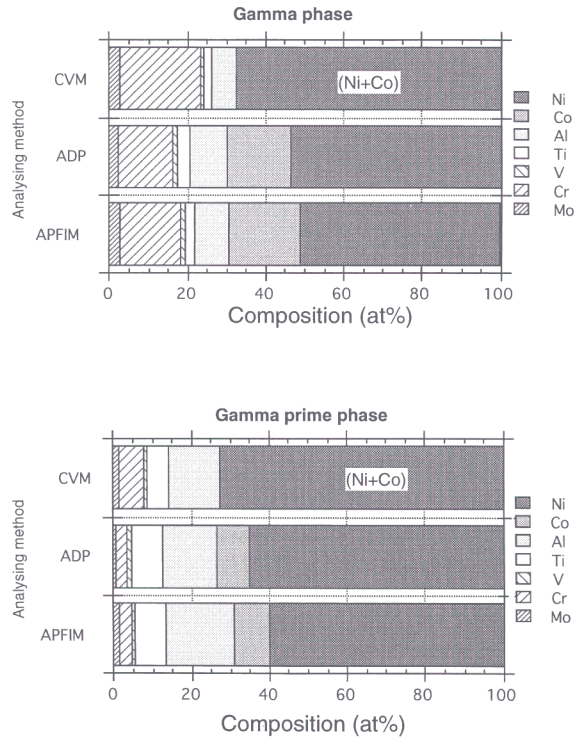


Fig. 3. The γ and the γ' phase composition of RR2000.

PHASE COMPOSITION OF CMSX4

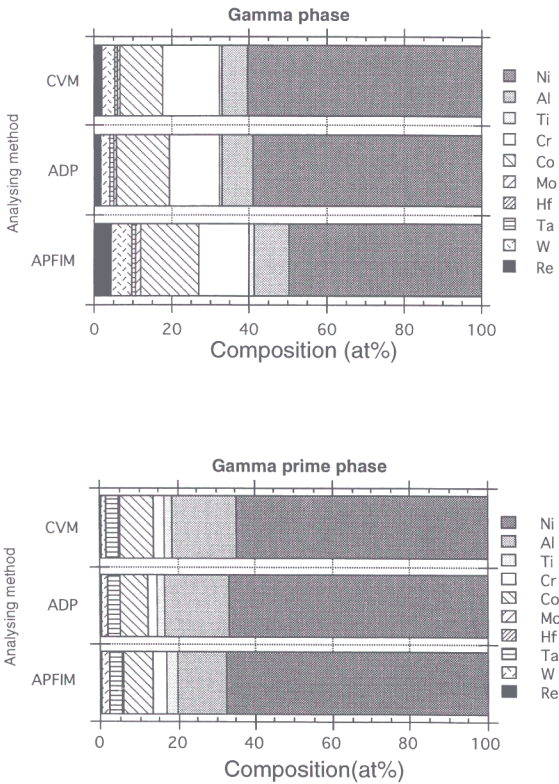


Fig. 2. The γ and the γ' phase composition of CMSX4.

3.2. Site occupation of alloying elements in the γ' phase

The location of atoms in the Ni-rich and mixed layers can be illustrated using a "ladder diagram". In this representation, the total number of aluminium atoms is plotted against the total number of nickel atoms collected during depth profiling. Thus, for pure fully-ordered Ni_3Al , the Ni layers would appear as horizontal lines on the ladder diagram, whereas the Al and Ni mixed layers would appear as lines inclined at 45°. This analysis was carried out for CMSX4; that for TMS63 is described elsewhere [10]. As described in previous reports [16,17], the probe hole was set off-centre away from the $\langle 100 \rangle$ pole to ensure that all atoms are collected from one plane before atoms are field evaporated from the next plane.

PHASE COMPOSITION OF TMS63

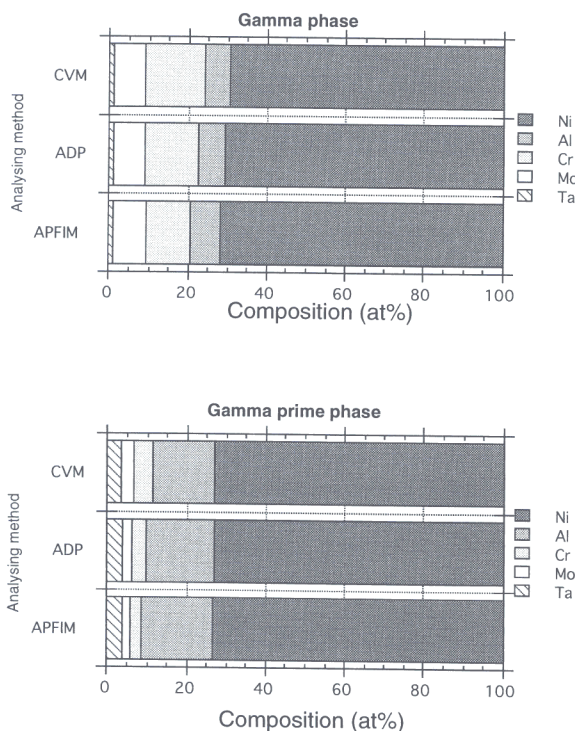


Fig. 4. The γ and the γ' phase composition of TMS63.

The size of the probe aperture was set to be smaller than the maximum geometrical size [17] so that the successive layer-by-layer analysis could be maintained even as the sample voltage increased in the range 14 to 19 kV.

The experimentally determined ladder diagram illustrated in Fig. 5 was analyzed quantitatively. More than 700 layers containing 30 000 ions were analyzed. The data are well behaved in the sense that the average number of ions detected per mixed layer (23.2) was found to be about the same as the corresponding number for the Ni layers (23.9). Site occupancies of alloying elements are calculated from the composition of each type of plane. Figs. 6 and 7 show the summarized site occupancy probabilities derived from APFIM analyses and CVM calculations. The experimental results confirm that W, Ta, Mo and Ti prefer to substitute for the Al sites, and show that this tendency is very strong for Ta, W and Mo

LADDER DIAGRAM FOR CMSX4

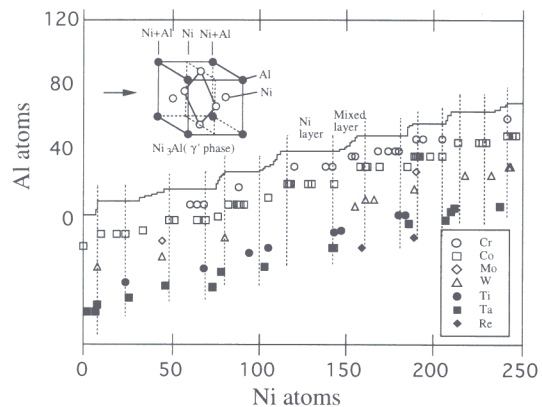


Fig. 5. The ladder diagram for CMSX4, indicating that Cr and Co preferentially substitute for Ni site whilst the other elements tend to occupy the Al site.

relative to Ti. Cr and Co clearly prefer the Ni sites, this preference being strongest for the Cr atoms. Although the concentrations of Re and Hf are small, our data appear to show with reasonable confidence that they all are much more likely to occupy the Al sites. These site occupation tendencies are in excellent agreement with data reported by Blavette et al. [12,14] and in good agreement with CVM except for Ti and Cr.

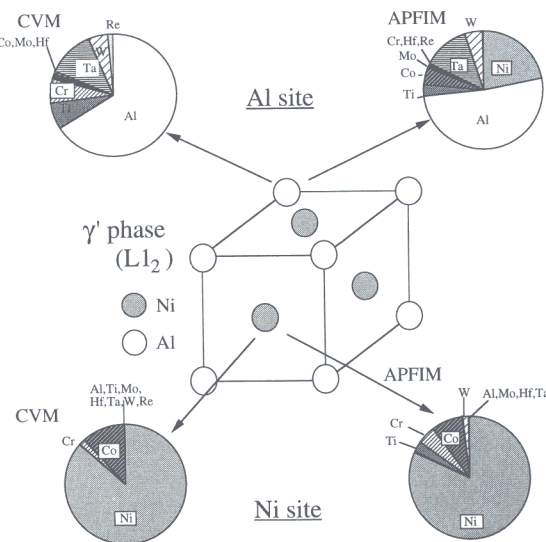


Fig. 6. The atomic configurations in the γ' phase of CMSX4.

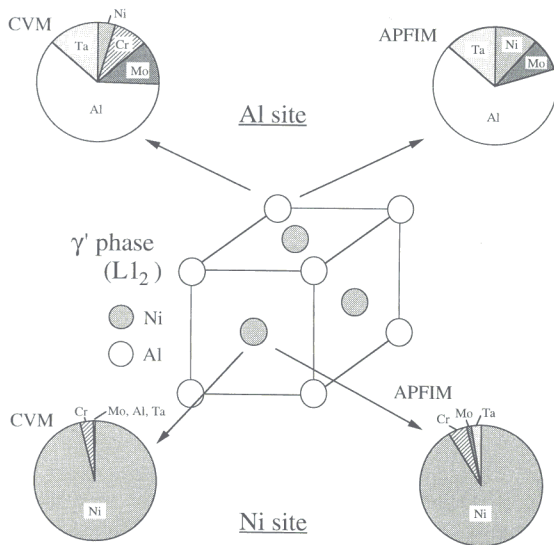


Fig. 7. The atomic configurations in the γ' phase of TMS63.

The behaviour of these elements, together with the fact that some Ni appears to substitute into the Al sites, requires further investigation.

According to Enomoto et al. [6,7], site occupancy in the γ' phase depends on the relative magnitude of the potential of each atom pair; in the case of Ta, for example, the Ni–Ta interaction is much stronger than the Al–Ta interaction. It is thus predicted that Ta will prefer to be substituted for Al and surrounded by Ni atoms. It is also predicted that Re, Hf, Mo and Ti, which have much more attractive pair potentials with Ni than Al, will be substituted for the Al site. APFIM investigations for CMSX4 and TMS63 confirm the validity of this prediction except for Ti, which requires further investigation.

Most elements which prefer to substitute for the Al sites in the γ' phase have relatively large atomic radii, such as Ta, Hf, Ti, Mo, W and Re. Among them, Mo, W and Re are partitioned into the γ phase. Enomoto and Harada reported [6] that for Ni–Al–X ternary alloys, the partition behaviour of Mo and W depends on the concentration of these elements which enrich in the γ phase with increasing concentration. This tendency to enrich in the γ phase becomes significant when some Cr is included with Mo and/or

W in a multi-component alloy, because of the deep pair potential of Cr–X in the γ phase [7]. It is also assumed that deep pair potential between Mo and W enhances this tendency to partition into the γ phase. This study confirmed that the partitioning and substitution behaviour of Re is similar to that of W and Mo.

The fact that large atomic radii elements Mo, W and Re are preferentially partitioned to the γ phase results in the relative expansion of the γ lattice parameter compared with the γ' . Consequently, the lattice misfit defined by $(a_{\gamma'} - a_{\gamma})/a_{\gamma}$, where a_{γ} is the γ lattice parameter etc., can be made negative by alloying with these three elements. Harada et al. [5,9] proposed, using ADP, that the creep rupture strength is strongly dependent on the lattice misfit and alloys with a large negative lattice misfit have excellent creep rupture properties, because they can easily form the so-called “rafter structure” and thus form the finer interfacial misfit dislocation network at high temperatures [19]. Indeed, the high Mo-containing (4.6 at%) alloy TMS-63, with a large negative lattice misfit at elevated temperatures, has an excellent creep rupture capability, and CMSX4, whose overall content of Mo, W and Re is 3.48 at%, comes next. Our experimental results confirm that the addition of alloying elements such as Mo, W and Re, which are likely to enrich in the γ phase and to occupy Al sites in the γ' phase, is one of the key factors in the design of alloys with high-temperature capabilities.

4. Conclusions

Investigations using atom-probe field ion microscopy were carried out to verify the results of computer simulations based on the alloy design program and the cluster variation method.

γ/γ' phase composition analyses confirm that Ti, Ta and Hf have a strong preference for the γ' phase, whilst elements such as Cr, Co, W, Re and Mo have a tendency to partition into the γ phase. V has a weak preference for the γ phase. These results agree very well with calculations.

The results obtained from the layer-by-layer analysis of the γ' phase generally confirm pub-

lished data and reveal that elements like Mo, Re, Ta and Hf have a strong preference, while Ti has a weak preference, for occupying the Al sites, whilst Co and Cr have a strong preference for Ni sites. These results are in good agreement with predictions from the CVM, except for Ti and Cr which require further investigation.

It appears that one of the key factors in improving the high-temperature capabilities of Ni-base superalloys is the addition of alloying elements such as Mo, Re and W, which prefer to dissolve in the γ phase rather than the γ' phase, and tend to substitute for the Al sites. This is because these particular elements give a large negative lattice misfit into superalloys.

5. Acknowledgements

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